

Hydrogen Production from Reforming of Cooking oil with CO₂ Removal Process

Watchrapong Inpakdee

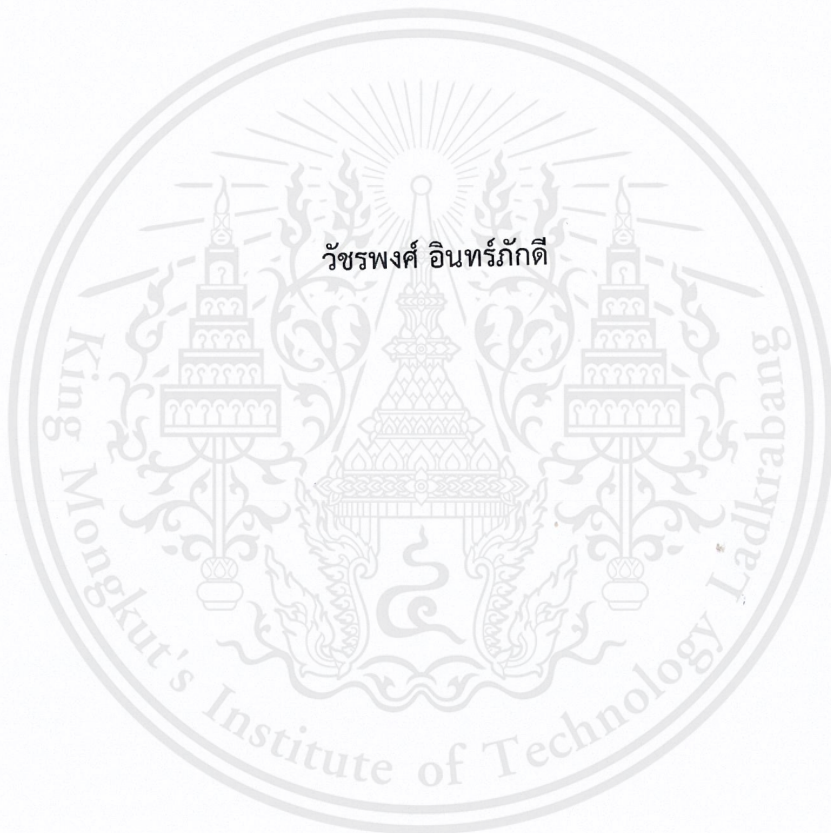


**A Report Submitted in Partial Fulfillment of the Requirements
for the Degree of Bachelor of Engineering (Petrochemical Engineering)
Department of Chemical Engineering, Faculty of Engineering,
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การผลิตไฮโดรเจนจากกระบวนการรีฟอร์มมิ่งน้ำมันที่ผ่านการใช้งาน
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Removal Process

By Watchrapong Inpakdee

Advisor Asst.Prof. Dr. Yaneeporn Patcharavorachot

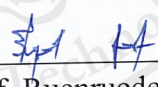
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Abstract

This project presents production process of hydrogen, as clean fuel, from cooking oil. The use of cooking oil has received much interest since it has low price. In addition, if hydrogen is produced from the used cooking oil, this is an alternative way to dispose of non-reusable waste. In this project, hydrogen production through autothermal reforming was investigated by considering four different cooking oils, i.e., fresh vegetable oil, used vegetable oil, fresh animal fat and used animal fat. It is noted that vegetable oil is soybean oil whereas animal fat is lard. This project aims to determine the optimal operating conditions for hydrogen production via thermodynamics calculation. Effects of oil types, steam to carbon molar ratio, reforming temperature and pressure and amount of calcium oxide on hydrogen production were examined. The results showed that the optimal operating conditions of reformer are temperature of 900 K, pressure of 1 bar and steam to carbon molar ratio of 5. Then, water gas-shift (WGS) reactor is installed after reforming process to enhance hydrogen content. It was found that the optimal operating conditions of WGS are at 360 K and atmospheric pressure. Furthermore, the chemical looping of calcium oxide is proposed in this process to remove carbon dioxide from synthetic gas. The simulation results showed that the optimal operating conditions of chemical looping are temperature of 777 K, pressure of 1 bar and amount of calcium oxide as 18 kmol/hr. Finally, the separator is used to separate steam. When the amount of hydrogen produced is analyzed, it can be concluded that the used soybean oil can produce the highest amount of hydrogen, followed by fresh soybean oil, used lard and fresh lard, respectively. Under these operating conditions, the hydrogen purity of 99.9% can be provided and this can be used as a liquid fuel in industries.

Keywords: Hydrogen, Used cooking oil, Autothermal reforming, Chemical looping

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เรื่อง การผลิตไฮโดรเจนจากกระบวนการรีฟอร์มมิ่งของน้ำมันที่ใช้ทำอาหาร
ร่วมกับกระบวนการแยกคาร์บอนไดออกไซด์

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สถาบันเทคโนโลยีพระจอมเกล้าเจ้าคุณทหารลาดกระบัง

บทคัดย่อ

โครงการนี้นำเสนอกระบวนการผลิตแก๊สไฮโดรเจนซึ่งเป็นเชื้อเพลิงสะอาดจากน้ำมันที่ใช้ทำอาหาร การใช้น้ำมันที่ใช้ทำอาหารมีความน่าสนใจเนื่องจากมีราคาถูก และถ้าแก๊สไฮโดรเจนผลิตมาจากน้ำมันที่ใช้งานแล้ว ก็จะเป็นอีกทางเลือกหนึ่งในกำจัดของเสียที่ไม่สามารถนำกลับมาใช้ใหม่ได้ โครงการนี้สนใจศึกษากระบวนการผลิตไฮโดรเจนด้วยกระบวนการออโตเทอร์มัลรีฟอร์มมิ่งโดยพิจารณาน้ำมันที่แตกต่างกัน 4 ชนิด ได้แก่ น้ำมันพืชใหม่ น้ำมันพืชที่ผ่านการใช้งานแล้ว ไขมันสัตว์ใหม่ และไขมันสัตว์ที่ผ่านการใช้งานแล้ว โดยในที่นี้น้ำมันพืชที่ใช้คือน้ำมันถั่วเหลือง ส่วนไขมันสัตว์ที่ใช้คือน้ำมันหมู ในการศึกษามุ่งเน้นหาสภาวะการดำเนินงานที่เหมาะสมในการผลิตแก๊สไฮโดรเจนโดยใช้การคำนวณทางเทอร์โมไดนามิกส์ ตัวแปรที่ศึกษาได้แก่ ชนิดของน้ำมัน อัตราส่วนโดยโมลระหว่างไอน้ำกับคาร์บอน อุณหภูมิและความดันในการทำปฏิกิริยาของกระบวนการออโตเทอร์มัลรีฟอร์มมิ่ง และปริมาณแคลเซียมออกไซด์ ผลการศึกษาแสดงให้เห็นว่าสภาวะการดำเนินงานที่เหมาะสมที่สุดของเครื่องรีฟอร์มเมอร์ คือที่อุณหภูมิ 900 เคลวิน ความดัน 1 บาร์ และอัตราส่วนโดยโมลระหว่างไอน้ำกับคาร์บอน เท่ากับ 5 จากนั้นจึงเพิ่มเครื่องปฏิกรณ์วอเตอร์แก๊สชิฟในกระบวนการรีฟอร์มมิ่งเพื่อเพิ่มปริมาณของแก๊สไฮโดรเจน พบว่าสภาวะการดำเนินงานที่เหมาะสมที่สุดคือ อุณหภูมิ 360 เคลวิน และความดัน 1 บาร์ เมื่อทำการแยกแก๊สคาร์บอนไดออกไซด์ด้วยกระบวนการเคมีคอลลูปปิ้งด้วยแคลเซียมออกไซด์ พบว่าอุณหภูมิและความดันที่เหมาะสมที่สุดในการดำเนินงานคือ 770 เคลวิน และ 1 บาร์ และปริมาณการใช้แคลเซียมออกไซด์ที่เหมาะสมที่สุดเป็น 18 กิโลโมลต่อชั่วโมง นอกจากนี้ยังทำการแยกไอน้ำออกจากแก๊สสังเคราะห์ด้วยเครื่องแยก เมื่อวิเคราะห์ปริมาณของแก๊สไฮโดรเจนพบว่าน้ำมันถั่วเหลืองที่ใช้แล้วให้แก๊สไฮโดรเจนได้ปริมาณมากที่สุด รองลงมาคือน้ำมันถั่วเหลืองบริสุทธิ์ น้ำมันหมูใช้แล้ว และน้ำมันหมูบริสุทธิ์ ตามลำดับ ซึ่งแก๊สไฮโดรเจนที่ผลิตได้มีความบริสุทธิ์สูงถึง 99.99 เปอร์เซ็นต์ สามารถนำไปทำเป็นเชื้อเพลิงเหลวในอุตสาหกรรมได้

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CHAPTER I

INTRODUCTION

1.1 Background [1-4]

Nowadays, energy plays a significant role in economic development in all countries. This leads to an increase in global energy demand. However, the consumption of fossil fuel-based energy encounters two main issues: (1) the depletion of fuel, resulting in the price crisis and (2) the emission of greenhouse and other gases to the atmosphere, leading to climate change. In order to solve these problems, hydrogen is regarded as an ideal energy source to replace the fossil fuel in the future since hydrogen is non-toxic and can be used as a fuel in the combustion engines without the emission of pollution.

In general, hydrogen can be produced through different processes, e. g. thermochemical, electrolysis and photolytic processes. Among these, thermochemical process is commonly used to produce hydrogen from hydrocarbon fuel. Today, 95% of hydrogen is produced from fossil fuels, such as natural gas and oil [1]. However, the use of fossil fuels as feedstocks was of interest to causes the problems as aforementioned. Therefore, the use of renewable resources has been interested in this project. Biomass is an efficient renewable energy since the use of biomass helps reduce dependence on fossil fuels. Biomass is a clean renewable energy source. It can be used to produce useful fuels, such as hydrogen, carbon dioxide, methane, and others. Currently, the use of cooking oil is one issue that must be handled. The advantage of hydrogen production from used cooking oil is high potential yields of hydrogen and low price [2] . Besides the vegetable oils, animal fats are also considering in this project. In addition to fresh vegetable oils and animal fats, the used cooking oil can be considered as one of feedstock. The use cooking oils is generated in large scale to be incapable of reusing because when it has been heated, it can cause some serious health hazards. The use of cooking oil may contain possibly carcinogenic free radicals. Interestingly, its price is cheaper compared to other biomass [3].

As mentioned above, hydrogen can be produced through thermochemical processes which are included steam reforming (SR), partial oxidation (POX), and the combination of steam reforming and partial oxidation commonly known as autothermal reforming (ATR). Comparison between advantages and disadvantages of

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each process, it is found that the autothermal reforming has received much attention since this process can produce hydrogen more than partial oxidation, whereas it requires the external energy less than the steam reforming [4]. For this reason, the autothermal reforming can provide high ratio of hydrogen to carbon monoxide and reduce the cost of production.

However, the gas products or synthesis gas obtained from autothermal reforming will contain high quantities of carbon dioxide. As a result, the concentration of hydrogen is reduced. Thus, the separation of carbon dioxide from synthesis gas is required to increase the purity of hydrogen. In the recent years, the carbon dioxide removal process based on the absorption process is considered in the industry. It can be divided into two types: (1) physical absorption process which is based on the bond between the molecules adsorbate on the surface of the absorbent and (2) chemical absorption process which involves a chemical reaction between the surface and the absorbate. This project focuses on the chemical absorption process. Chemical looping has a significant advantage compared to another absorption technologies since chemical looping is used for capture carbon dioxide with a low energy demand. Moreover, the absorbent can be regenerated.

This project aimed to develop a model of the hydrogen production process through autothermal reforming of fresh and used vegetable oils/ animal fats integrated with the chemical looping process. AspenPlus™ software was used to design and simulate the process to produce hydrogen.

1.2 Objective

To study and simulate the hydrogen production process through autothermal reforming integrated with chemical looping using calcium oxide (CaO) as absorbent by using different feedstocks (i.e., fresh and used vegetable oil and fresh and used animal fat).

1.3 Scope of Work

1.3.1 Develop the hydrogen production process through autothermal reforming by using AspenPlus™ simulation software and compare the simulation results with the experimental data obtained from the literatures.

1.3.2 Simulate hydrogen production process through autothermal reforming by considering the effect of important parameters on hydrogen production and energy consumption. The considered parameters are as listed below:

- Type of feedstocks: fresh vegetable oil, used vegetable oil, fresh animal fat and used animal fat
- Temperatures in reformer: 800-1,000 K
- Pressures in reformer: 1-5 bar
- Temperatures in Water gas shift reactor: 300-400 K
- Steam to carbon molar ratios: 1-5
- Temperatures in absorber: at 600-800 K
- Calcium oxide to carbon monoxide ratio: 1-5

1.3.3 Develop the hydrogen production process through autothermal reforming integrated with chemical looping using calcium oxide as absorbent. The effect of absorbent to carbon molar ratios in a range of 0.1-1 on hydrogen production and energy consumption is examined.

1.4 Expected Outputs

1.4.1 The flowsheet of hydrogen production through autothermal reforming from various types of edible oil was obtained and can be further used to investigate and develop the hydrogen production process.

1.4.2 The optimal operating conditions for hydrogen production from edible oil could be provided.

1.4.3 The hydrogen production from used cooking oil could reduce the disposal and add value of used cooking oil.

CHAPTER II LITERATURE REVIEWS

2.1 Alternative energy [5-6]

Renewable energy or alternative energy is energy derived from natural resources. This includes sunlight, wind, rain, geothermal heat, and various forms of biomass. Figure 2.1 shows the total energy consumption classified by types of energy resource and be found that renewable energy is used only 10% [6]. The main purpose of using renewable energy is to replace the fossil fuels having environmental impact. The use of renewable fuel can reduce greenhouse gas emissions since it will reduce carbon dioxide emissions from other hydrogen production (i. e. coal, petroleum, natural gas).

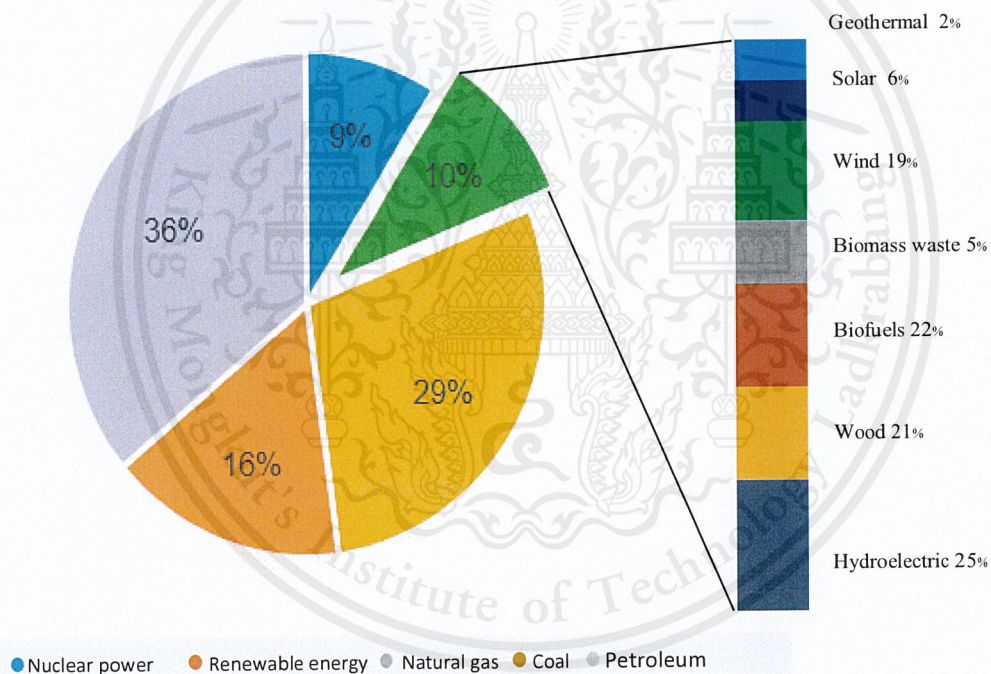


Figure 2.1. The energy consumption by energy source, 2015 [6].

2.2 Biomass [7]

Biomass is an organic material that comes from plants or animals. It is perceived as the most promising of renewable sources. Biomass can be converted into liquid biofuels and biogas that can be further used as fuels. In addition, it can be converted to other useable forms like methane, hydrogen, carbon monoxide, and others. Sources of biomass are considering as follows.

- Vegetable, such as palm, corn, cane, cassava, legumes and sun flower seed.
- Residual waste, such as straw, bran, sawdust, wood chips and Bark.
- Waste from the community, such as used cooking oil and dung.

2.3 Vegetable oil [8]

Vegetable oil can be produced from various type of plants; for example, peanuts, soybeans, sunflower seed and palm oil. Chemically, vegetable oil is an ester of glycerin and three long-chain fatty acids. It is commonly referred to as a 'triglyceride'. All triglycerides have the same glycerin unit. It is the fatty acids that contribute to the different properties of the various vegetable oils (Figure 2. 2) . Vegetable oil is used in this study contained mainly triglycerides and long-chain fatty acids. The fatty acids of fresh cooking oil contain mainly palmitic acid and linoleic acid, as shown in Table 2.1.

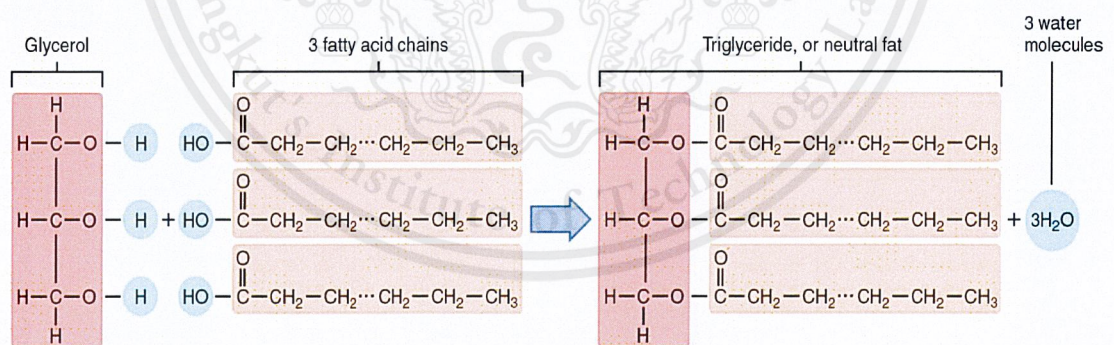


Figure 2.2. Three fatty acid chains are bound to glycerol by dehydrogenation synthesis [8].

Table 2.1 Main compounds of feedstocks

Fatty acids	Chemical structure	Mass fraction (%)			
		Fresh vegetable oil (FVO)	Used vegetable oil (UVO)	Fresh animal fat (FAF)	Used animal fat (UAF)
Palmitic	C16:0	0.1058	0.104	0.29	0.2239
Stearic	C18:0	0.0476	0.0451	0.15	0.1281
Oleic	C18:1	0.2252	0.2437	0.45	0.4253
Linoleic	C18:2	0.5234	0.519	0.1	0.1207
Linolenic	C18:3	0.0819	0.0652	-	0.0081

Besides fresh cooking oil, hydrogen production from the used cooking oil is also interested. In general, the used cooking oil should not be employed repeatedly in several times because it will be loss both physical and chemical properties. When unsaturated fatty acid from cooking oil is heated, its color will be changed from yellow to brown or black. Furthermore, used cooking oil is highly toxic if it is used as eating activities, it can increase risk of various diseases, such as heart disease, cancer and diabetes.

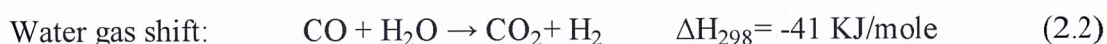
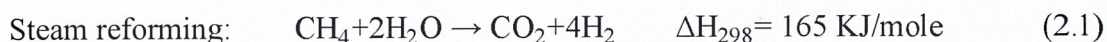
Table 2.1 also shows the main components of fresh and used cooking oil [9]. It can be seen that used vegetable oil mainly contains linoleic acid (51.9 %), oleic acid (24.37 %), palmitic acid (10.4 %), linolenic acid (6.52 %) and stearic acid (4.51 %). This information shows a deformation of structure. The major deformation of structure is attributed to the thermal degradation of the unsaturated fatty acid includes linoleic acid and linolenic acid.

2.4 Hydrogen production [10-19]

In general, hydrogen production can be divided into three main processes that include steam reforming (SR), partial oxidation (POX) and the combination of steam reforming and partial oxidation commonly known as autothermal reforming (ATR). Each process can be described as below.

2.4.1 Steam reforming [10-16]

Steam reforming is endothermic reaction and thus, the external heat source is significantly required. Feedstock will be reacted with steam in the presence of a catalyst to produce hydrogen and carbon monoxide through the steam reforming reaction. Then, carbon monoxide is further reacted with the residual steam to produce more hydrogen and carbon dioxide through water gas shift reaction. Eqs. (2.1) and (2.2) show the example of steam reforming reaction of methane.



2.4.2 Partial oxidation [17]

Partial oxidation is a chemical reaction that occurs when a mixture of the feedstock and pure oxygen (O_2) are reacted under high temperature. The partial oxidation process is exothermic reaction. Although this process can eliminate the requirement of external energy source and be fast start-up, it has a high cost of production since the air separator is needed to produce oxygen. In addition, it can provide hydrogen lower than steam reforming process. Eqs. (2.3) to (2.5) show the example of partial oxidation reaction of methane.

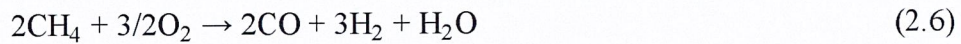
Partial oxidation reaction:



2.4.3 Autothermal reforming [18-19]

Autothermal reforming is a combination of steam reforming and partial oxidation. In this process, hydrocarbon fuel will react with oxygen and steam. Since both endothermic and exothermic reactions occur in the single reactor, the heat balance is an important issue which should be taken into consideration. In order to achieve the heat balance in the system without requirement of external energy source, the heat released from the partial oxidation must be high enough to supply to the steam reforming. The main advantages of autothermal reforming is that it can provide

higher hydrogen than partial oxidation and require less energy consumption than steam reforming. The example of autothermal reforming reaction of methane is expressed in Eq. (2.6).



2.5 Carbon dioxide separation [20-22]

In general, the gas product obtained from reforming process will be contained underside product, such as carbon dioxide, carbon monoxide, methane, water and others. From the literature survey, it is found that the gas product from the autothermal reforming process will contain large quantities of carbon dioxide which results in the greenhouse effect as well-known. Therefore, the carbon dioxide separation should be installed in the hydrogen production process [20].

There are several techniques to separate carbon dioxide from the gas product. These include absorption, adsorption, cryogenics, membrane, and others [21]. The choice of these techniques depends on the characteristics of gas product released. Currently, the most commonly encountered use of the absorption since it has a high efficiency to trap carbon dioxide and non-corrosive equipment.

2.5.1 Absorption process

Absorption process involves atoms or molecules crossing the surface and entering the volume of the material. The most commonly encountered use of absorption is for the separation and purification of a gas mixture. The absorption is divided into two types, including physical and chemical absorption [21].

Physical absorption of the gas mixture in a liquid solvent involving mass transfer occurs at the interface between gas and liquid. The rate and amount of absorption also depend on physical properties of liquid or gas like solubility, temperature, pressure and surface area of the interface. Chemical absorption is a chemical reaction between the absorbed and the absorbent substances. Sometimes it combines with physical absorption. Chemical absorption depends on stoichiometry of the reaction and the concentration of its reactants.

2.5.2 Chemical looping [22]

Chemical looping is regarded as ideal method to reduce the carbon dioxide emissions to surrounding in the near future since this method can capture carbon dioxide with a low energy demand. In this project, the chemical looping will be used to absorb carbon dioxide by using calcium oxide (CaO) based sorbents. The reaction considered in the calcium looping reactions are shown below:



Figure 2.3 shows the calcium looping process which consists of two reactors, including carbonator and calciner. In the carbonator, carbon dioxide reacted with calcium oxide and then, calcium carbonate or be called limestone is produced through carbonation reaction, as expressed in Eq. (2.7). In a subsequent thermal regeneration called calcination, calcium carbonate is regenerated to separate carbon dioxide as show in Eq. (2.8).

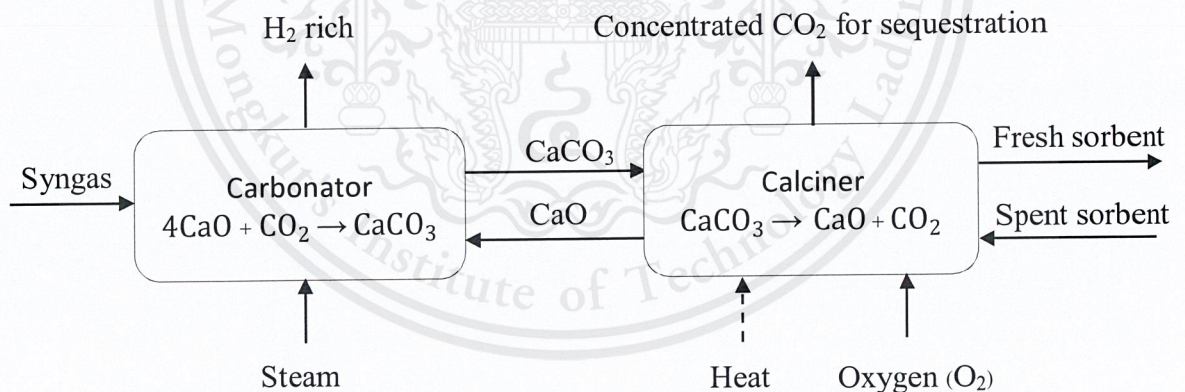


Figure 2.3. Schematic of carbon dioxide capture by using calcium looping.

2.6 Related research

Kim [10] presented the use of vegetable oil for producing synthesis gas or syngas. Vegetable oil used as feedstock can be classified in two types that include fresh cooking oil (FCO) and waste cooking oil (WCO) derived from used oil. He characterized the component of both feedstock and found that FCO contains mainly palmitic acid (8.6%) and linoleic acid (83.5%), whereas WCO is composed of palmitic acid (9.9%), linoleic acid (33.6%), oleic acid (30.3%) and stearic acid (3.7%). The presence of oleic and stearic acid in WCO will be attributed to the decomposition of linoleic acid by decarboxylation and hydrogenation during the cooking process of FCO. The experimental result indicated that, concentrations of producer gases (i.e., H_2 , CO , and CH_4) obtained from WCO gasification were higher than those obtained from FCO due to the decomposition of linoleic acid in the fuel properties of WCO. In addition, the experiments were carried out using an activated carbon filter to reduce tar content.

Rafiq [19] presented the experimental study of hydrogen production through autothermal reforming from used cooking oil. In the experiment, the reaction was carried out under atmospheric pressure at 800-1000 K. In addition, propane is used in the oxidation to maintain autothermal reforming operation. The addition of propane can improve the stability of the autothermal reforming process. It was found that concentration of hydrogen and carbon dioxide increasing, carbon monoxide and methane concentrations decreasing with an increase in the steam flow rate. This could be explained by a combination of three phenomena. Firstly, when the steam flow rate increase, the heat transfer from oxidation sites to steam reforming sites would be increased. Secondly, when the reformer operates at low steam to carbon molar ratio, the occurrence of catalyst deactivation was more likely. Finally, when the reformer was operated at high steam to carbon molar ratio, the equilibrium of the water gas shift reaction moved forward and the production of carbon dioxide is more pronounced compared to that of carbon monoxide. In addition, an increase in the reaction temperature resulted in the production of smaller species (i.e., H_2 , CO , CO_2 and CH_4), but the concentration of higher species (hydrocarbons with high molecular weight) is decreased. If the operation is at low temperature, the hydrogen and carbon dioxide yields are low. This result was due to the formation of methane as the hydrogenation of carbon monoxide and coke.

CHAPTER III

RESEARCH METHODOLOGY

This project aimed to compare hydrogen production through autothermal reforming by using different cooking oils. This factor included fresh and used vegetable oil and fresh and used animal fat. The Aspen Plus™ software was used to design and simulate the hydrogen production. Section 3.1 presents the diagram of hydrogen production through autothermal reforming whereas Section 3.2 shows the intergrated system of autothermal reforming and chemical looping process. Finally, the simulation approach is described in Section 3.3.

3.1 Hydrogen production by autothermal reforming of cooking oil

The hydrogen production from cooking oil will be operated with multiple reactors: autothermal reformer and water gas shift reactor. The mixture of cooking oil and reforming agent is further supplied to ATR reactor. After that, WGS reactor is installed after reforming process to enhance hydrogen content as show in Figure 3.1. The unit models and operating conditions used are listed in Table 3.1.

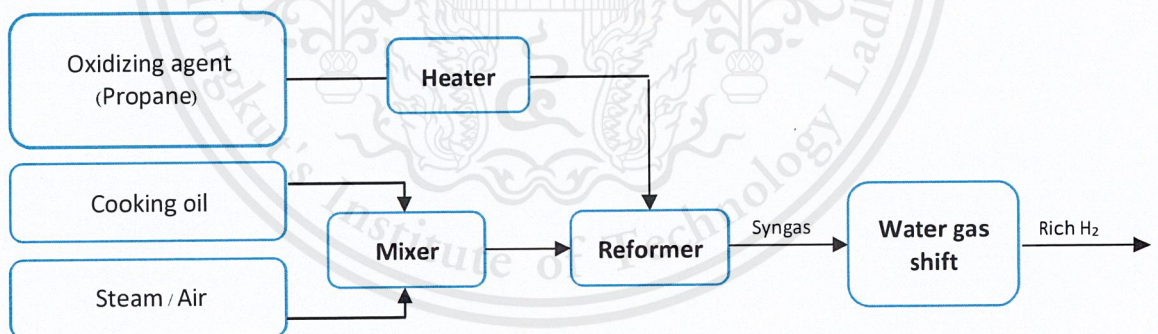


Figure 3.1. Diagram of hydrogen production by autothermal reforming.

Table 3.1 Unit operation models and operating conditions of reforming

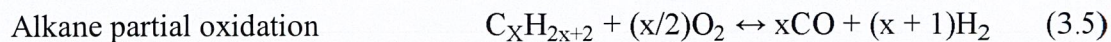
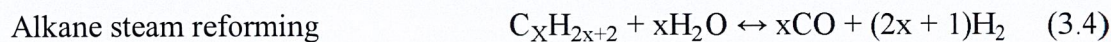
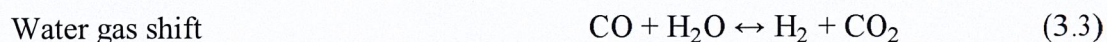
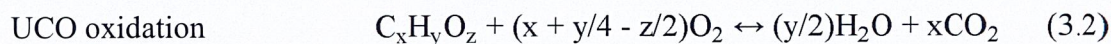
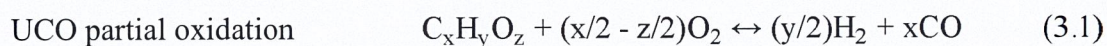
Unit operation	Unit model	Operational range
Mixer	Mix	200-400 K
		1 bar
Heater	Heater	600 K
Reformer	RGibbs Reactor	800-1000 K
		1 bar
Water gas shift	REquil Reactor	300-400 K
		1-5 bar

3.1.1 Feedstock

Cooking oil and reforming agent (steam and air) is separately entered into the mixer. The cooking oils considered in this project are fresh and waste vegetable oil and fresh and waste animal fat. In general, the waste cooking oil samples have been thermally treated at high temperature and therefore, it is possible to contain a contamination of ash, char, or residue remaining from frying which it has to be filtered before being used as a substrate. However, in this research, the waste cooking oil will be assumed to pass the filter successfully.

3.1.2 Reformer

The mixture of cooking oil and reforming agent is further supplied to reformer simultaneously with propane heated by heater. The possible reaction can be occurred in the reformer, as given in Eqs. (3.1)-(3.11)





3.2 Carbon dioxide absorption by calcium looping

The absorption process is widely used for the separation and purification of a gas mixture. This process can separate contaminants, i.e. carbon monoxide, steam, carbon dioxide from synthesis gas to increase the purity of hydrogen. In this project, the chemical looping process is used to absorb carbon dioxide by using calcium oxide (CaO) based sorbents. The absorption diagram is shown in Figure 3.2. The unit models and operating conditions of carbon dioxide absorption are summarized in Table 3.2.

3.2.1 Feedstock

Feedstock for the adsorption process consists of the synthesis gas obtained from autothermal reforming process.

Table 3.2 Unit operation models and operating conditions of the absorption

Unit operation	Unit model	Operational range
Absorber	Mix	800-1000 K
		1 bar
Flash	Heater	300-400 K
Regenerator	RGibbs Reactor	1000-1200 K
		1 bar

3.2.2 Absorber and Regenerator

Chemical looping process consists of two reactors; absorber and regenerator. The absorber is used to separate carbon dioxide from the synthesis gas by using calcium oxide based sorbents. In the absorber, carbon dioxide reacts with calcium oxide and produces calcium carbonate through carbonation reaction. After that, calcium carbonate is directly supplied to the regenerator where rich carbon dioxide is separated from calcium oxide through calcination reaction. In addition, the flash separator is employed to increase hydrogen concentration by extracting water from rich hydrogen.

3.3 Simulation approach

Figure 3.3 presents the simulation approach for hydrogen production through autothermal reforming integrated with chemical looping process. Aspen PlusTM software is used to design and simulate the hydrogen production process, as show in Figure 3.4. In the process simulation, the thermodynamic analysis was performed based on the property method of UNIF-LBY. This method can be used for triglycerides. When the operating conditions of reformer (i. e. T_{ref} , P_{ref} , SCR, OCR) and composition of feedstock and reforming agent are specified simultaneously with the operating conditions of absorption process (i. e. T_{ref} , P_{ref} , SCR, OCR), the equilibrium product composition can be calculated based on the total Gibbs free energy minimization method. The molar ratio between reforming agent (steam and air) feedstock can be calculated from Eqs. (3.10) and (3.11). In this project, the effect of important parameters (e. g., type of feedstock, reformer temperature, SCR and OCR) is investigated in terms of H_2 mole fraction.

$$\begin{aligned} &\text{Steam to carbon ratio (SCR)} \\ &= \left(\frac{\text{mole of steam}}{\text{mole of cooking oil reacted}} \right) / \left(\frac{\text{mole of steam}}{\text{mole of cooking oil reacted}} \right)_{\text{stoichiometric}} \end{aligned} \quad (3.10)$$

$$\begin{aligned} &\text{Steam to carbon ratio (OCR)} \\ &= \left(\frac{\text{mole of steam}}{\text{mole of cooking oil reacted}} \right) / \left(\frac{\text{mole of steam}}{\text{mole of cooking oil reacted}} \right)_{\text{stoichiometric}} \end{aligned} \quad (3.11)$$

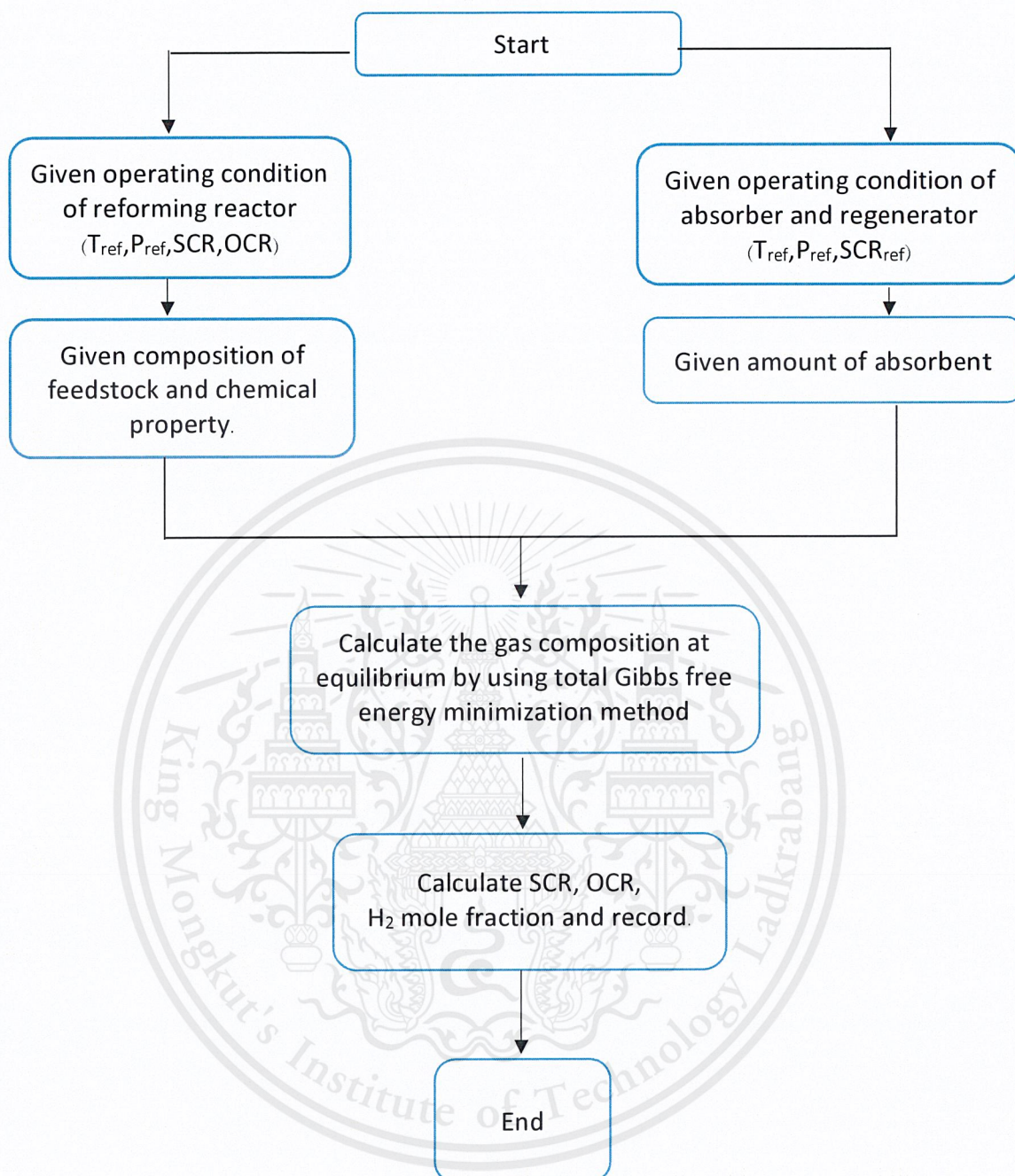


Figure 3.3. Diagram of the hydrogen production.

CHAPTER IV

SIMULATION RESULTS AND DISSCUSION

The simulations results of hydrogen production can be divided into 3 major parts. Section 4.1 presents the comparison between simulation result and experimental data from other research. This section was used to verify the reliability of the process simulation. Section 4.2 shows the results of hydrogen production through autothermal reforming integrated with chemical lopping using calcium oxide. This section aims to determine the optimal operating conditions for hydrogen production. This section can be divided into 2 subsections. Section 4.2.1 presents the effect of changes in the operating conditions of the reformer that include temperature and pressure of reformer, steam to carbon molar ratio (S/C), temperature and pressure of water gas shift unit on hydrogen production. Section 4.2.2 shows the effect of changes in the operating conditions of the absorption unit that include temperature and pressure of absorber and amount of absorbent on carbon dioxide removal. Finally, Section 4.3 shows the effects of oil types in hydrogen production from autothermal reforming unit at different temperatures and pressures of reformer.

4.1 Comparison results between simulation and experimental results

The reliability of the process model in this project was observed by comparing with the experimental data from Rafiq and Hustad [19] under same operating conditions. They studied the use of vegetable oil as feedstock for hydrogen production through autothermal reforming. Under same operating conditions as temperature of 850 K, pressure of 1 bar, steam to carbon molar ratio of 1 and oxygen flow rate of 369.84 NL/hr, the mole fractions of each component at different water flow rates obtained from simulation and experiment were compared, as shown in Figure 4.1. It can be seen that the simulation results are agree with the experimental data. Therefore, the process model is reliable for studying the effect on hydrogen production from autothermal reforming.

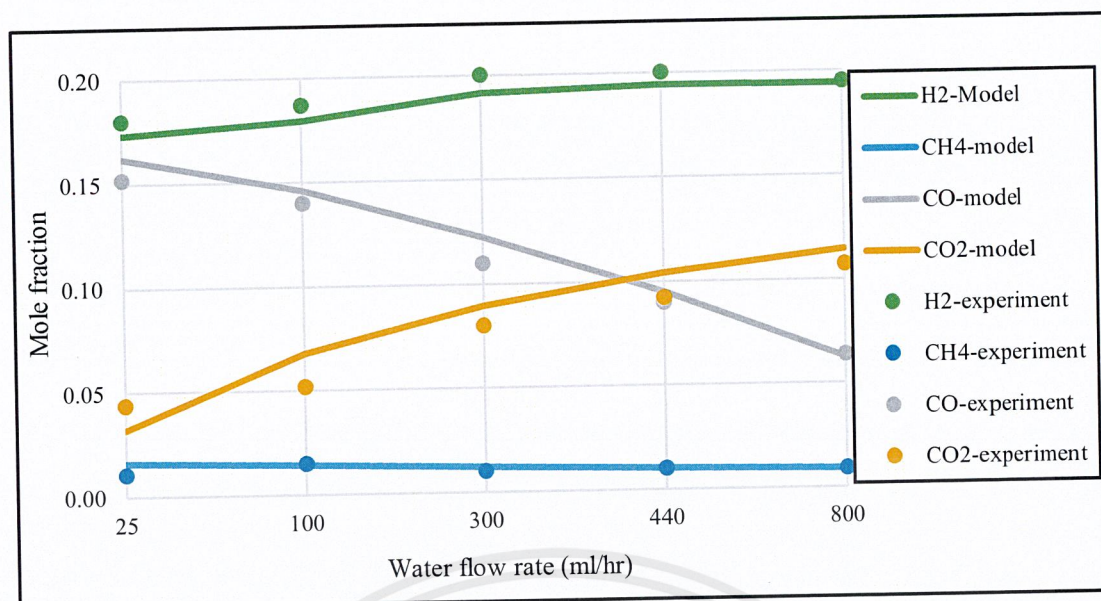


Figure 4.1. Comparison of the molar ratios of each component between the simulation results and the experimental data. of Rafiq and Hustad [19].

4.2 Effect of operating conditions on hydrogen production

This section presents the effect of operating condition of autothermal reformer and absorber on hydrogen production by considering used vegetable oil. The used vegetable oil which is composed of linoleic acid (51.9 %), oleic acid (24.37 %), palmitic acid (10.4 %), linolenic acid (6.52 %) and stearic acid (4.51 %) is fed into the reformer with 1 kmole/hour. The operating parameters are listed in Table 3.1. The standard operating conditions of reformer are temperature of 800 K, pressure of 1 bar and steam to carbon molar ratio of 5.

4.2.1 Effects of operating condition in reformer

4.2.1.1 Effects of temperature in autothermal reformer

Figure 4.2 shows the effect of temperature and pressure of autothermal reformer on hydrogen production. When the effect of reformer temperature is considered, it can be seen that hydrogen production increases with increasing temperature in the range of 800 to 1,000 K at a fixed steam to carbon molar ratio of 5. This is since ATR is endothermic reaction [19], equilibrium shifts towards products side with increasing temperature and this results in an increase in hydrogen production. The simulation result indicates that the maximum hydrogen content can be obtained when the reformer is operated at 900 K.

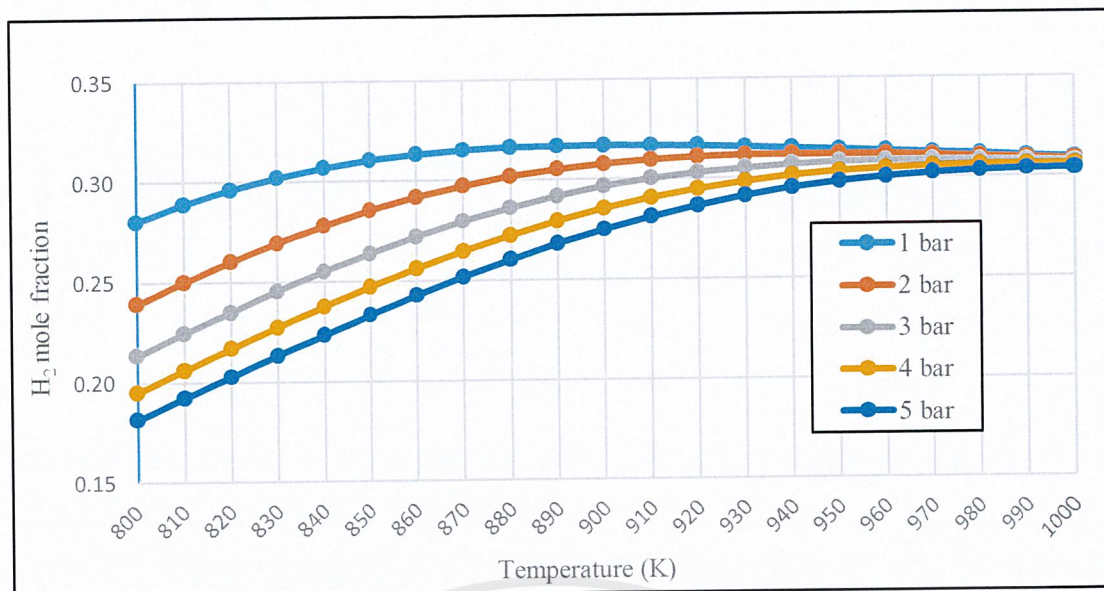


Figure 4.2. Effects of changing the temperature and pressure in autothermal reformer at S/C of 5 on hydrogen mole fraction.

4.2.1.2 Effects of pressure in autothermal reformer

From Figure 4.2, it is found that hydrogen production decreases with increasing pressure in the range of 1-5 bar at a fixed temperature of 900 K and steam to carbon molar ratio of 5. The simulation result indicates that hydrogen production increases with decreasing pressure of reformer to atmospheric pressure or 1 bar. This is because pressure of product side has higher pressure than reactant side [10]. So, if pressure is increased, equilibrium will shift towards the lower pressure side. The gas products will be consumed by reverse reaction and reactants will form. As a result, the production of hydrogen will be decreased. So, the high pressure has negative influence on the hydrogen production, ATR process should be operated close to atmospheric pressure.

4.2.1.3 Effects of S/C in autothermal reformer

The effect of S/C on hydrogen production at temperature of 900 K and pressure of 1 bar is shown in Figure 4.3. In general, amount of hydrogen was found to increase with increasing S/C in the range between 1-5 at a fixed temperature and pressure. Since an increase in S/C means that the mole number of steam in reactant side is higher, the equilibrium of ATR reaction shifts towards the products side (Eq.3.4) which leads to the increased hydrogen production. Moreover, The increase of S/C also promotes the reverse methanation reaction (Eqs.(3.8)-(3.9)) and this results in higher hydrogen production.

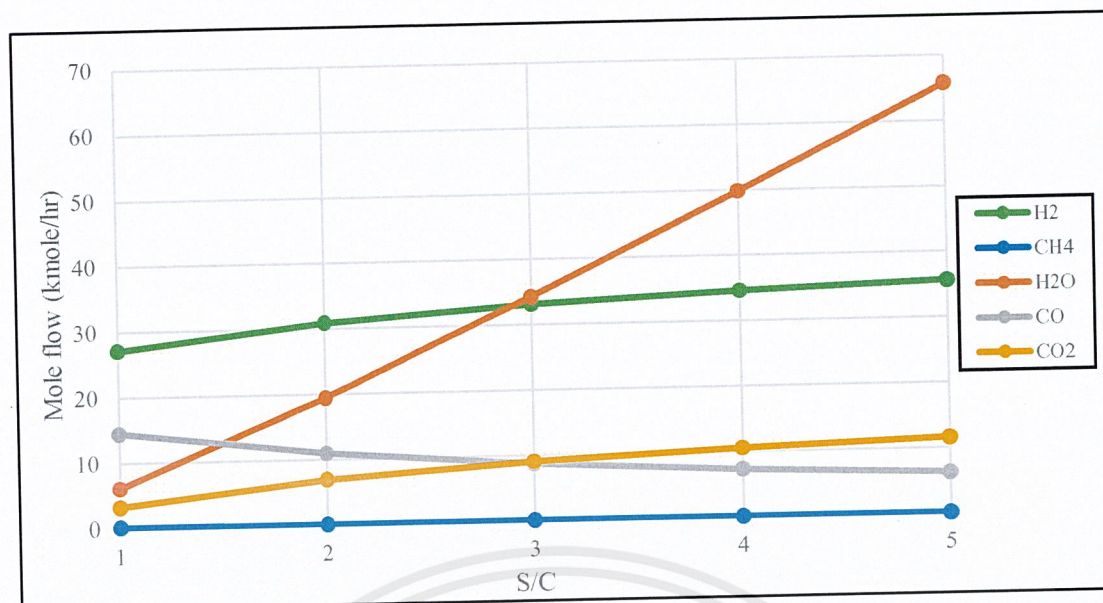


Figure 4.3. Effects of changing the steam to carbon molar ratio in autothermal reforming reactor on mole flow of each component at temperature of 900 K and pressure of 1 bar.

4.2.1.4 Effects of temperature and pressure in water gas shift reactor

Figure 4.4 shows the effect of temperature and pressure of WGS reactor on hydrogen production. When the effect of temperature is considered, it can be seen that hydrogen production increase with increasing temperature in the range of 300 to 360 K at a fixed S/C of 5. This is since most of the reaction in the WGS reaction is exothermic reaction [15], equilibrium shifts towards products side with low temperature. In addition, the high pressure has negative influence on the hydrogen production. This is because pressure of product side has higher pressure than reactant side. The gas products will be consumed by reverse reaction and reactants will form. As a result, the production of hydrogen will be decreased. The simulation result indicates that the maximum hydrogen content can be obtained when the WGS reactor is operated at 360 K at atmospheric pressure.

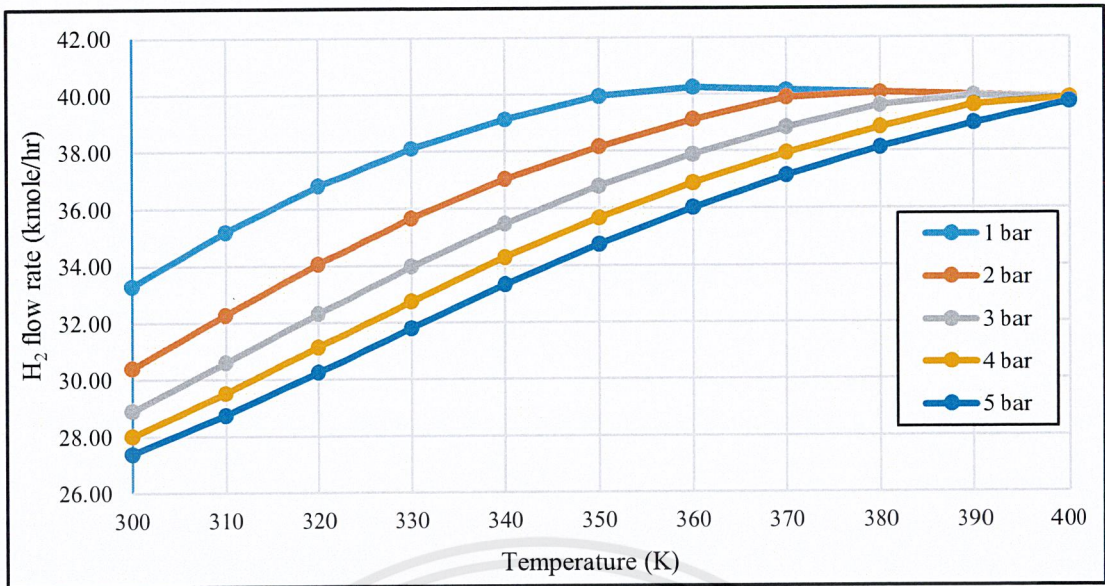


Figure 4.4. Effects of changing the temperature and pressure in water gas shift reactor on hydrogen mole flow rate.

4.2.2 Effects of operating condition in absorber

4.2.2.1 Effects of temperature in absorber

The effect of absorber temperature on the mole fractions of carbon dioxide and hydrogen is shown in Figures 4.5 and 4.6, respectively. Effect of temperature in range of 600-800 K is investigated whereas pressure is fixed at 1 bar. As seen in Figure 4.5, the carbon dioxide mole fraction increases with increasing temperature. This is due to the fact that the carbamation reaction occurred in absorber is exothermic reaction (Eq. (2.7)) and thus, the reduction of CaO to CaCO₃ is significantly restrained by thermodynamics and kinetics at high temperature. In addition, when carbon dioxide is separated from gas production, equilibrium of reaction will shift towards products side to increasing hydrogen production as shown in Figure 4.6. From the simulation result, the optimal absorber temperature is 660 K.

4.2.2.2 Effects of the amount of calcium oxide in absorber

Figures 4.5 and 4.6 demonstrate the effect of amount of CaO on the mole fractions of carbon dioxide and hydrogen. At fixed temperature, it can be observed that increases of amount of CaO can decrease carbon dioxide content whereas hydrogen content can be improved. This is because more CaO added into the absorber can react with carbon dioxide in synthesis gas; therefore, decrease of carbon dioxide and increase of hydrogen are presented.

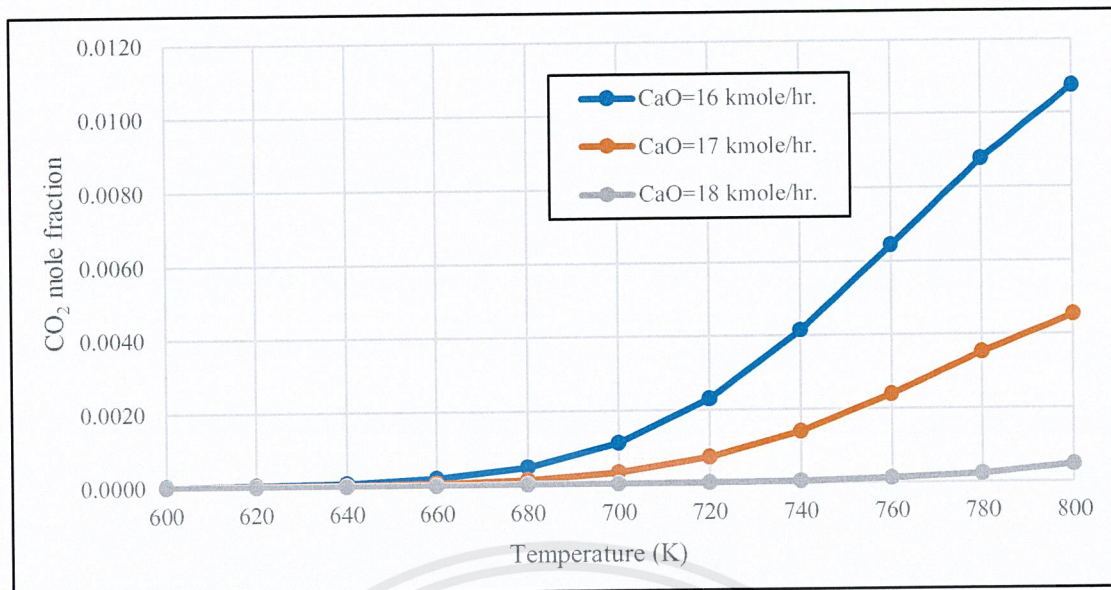


Figure 4.5. Effects of changing the temperature and amount of calcium oxide in absorber at 1 bar on carbon dioxide mole fraction.

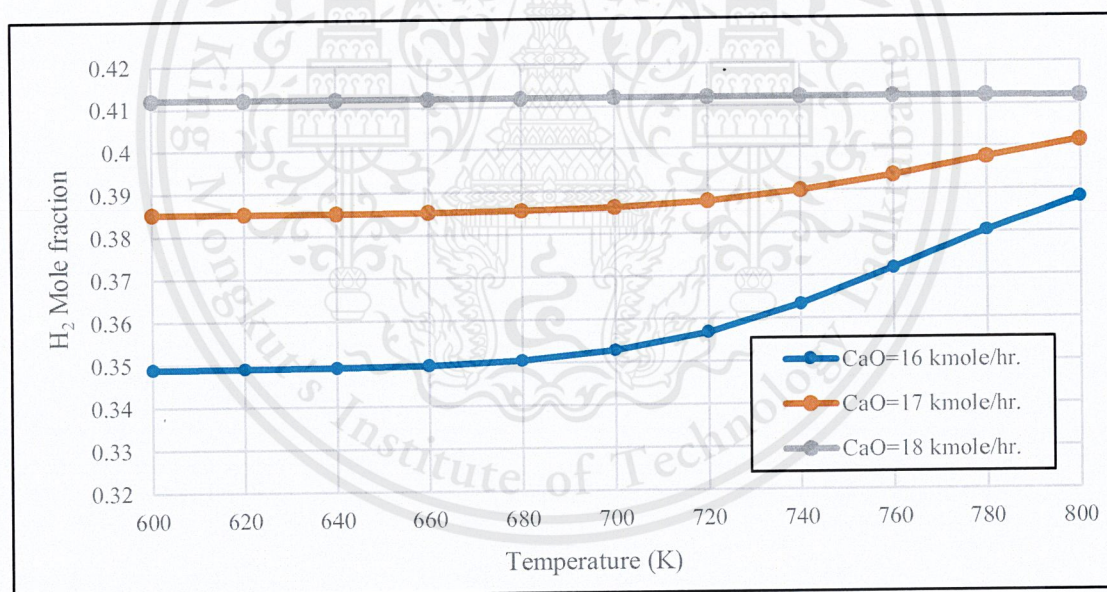


Figure 4.6. Effects of changing the temperature and amount of calcium oxide in absorber at 1 bar on hydrogen mole fraction.

4.3 Effect of oil types on hydrogen production

In this section, the influence of using different oil types, i.e., fresh vegetable oil (FVO), used vegetable oil (UVO), fresh animal fat (FAF) and used animal fat (UAF) on hydrogen production is presented. It is noted that the vegetable oil is soybean oil whereas animal fat is lard. The hydrogen production as a function of different reformer temperature, steam to carbon molar ratio and water gas-shift reactor temperature is shown in Figures 4.7-4.9, respectively. All results are consistent that used vegetable oil can produce the highest amount of hydrogen, followed by used animal fat, fresh vegetable oil and fresh animal fat. In the point of chemical, vegetable oil is an ester of glycerin and three long-chain fatty acids, and is commonly referred to a triglyceride. All triglycerides have the same glycerin unit, so it is the fatty acids that contribute to the different properties of the various vegetable oils which mainly component of vegetable oil is long chain hydrocarbon of fatty acids compared with animal fat such as oleic acid and palmitic acid. The used vegetable oil can produce the highest amount of hydrogen since used vegetable oil was heated to elevated temperature. It may cross chemical reactions, hydrolysis, oxidation and polymerization. Degradation products such as free fatty acids. Besides, the viscosity of the cooking oil will increase and its color will go darker [24].

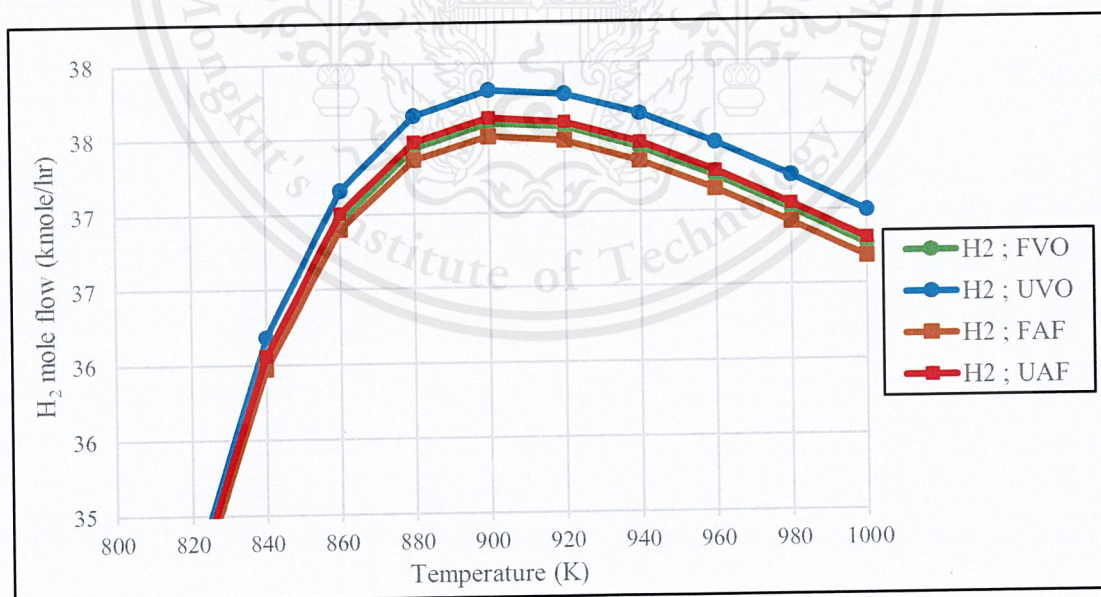


Figure 4.7. Effects of changing the temperature and type of cooking oils in ATR reactor on hydrogen mole flow.

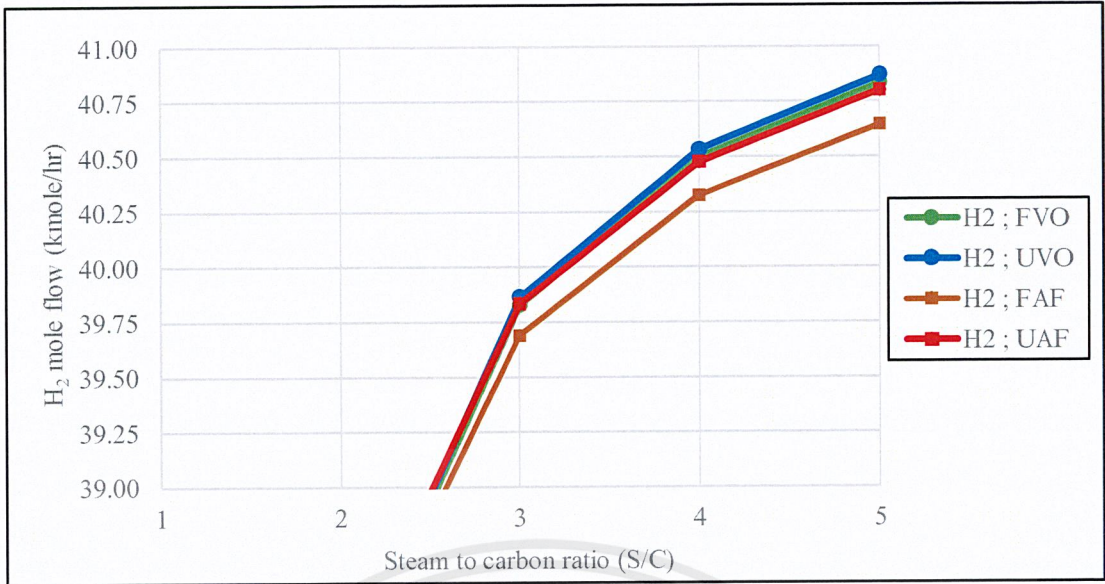


Figure 4.8. Effects of changing the steam to carbon molar ratio and type of cooking oils in ATR reactor on hydrogen mole flow.

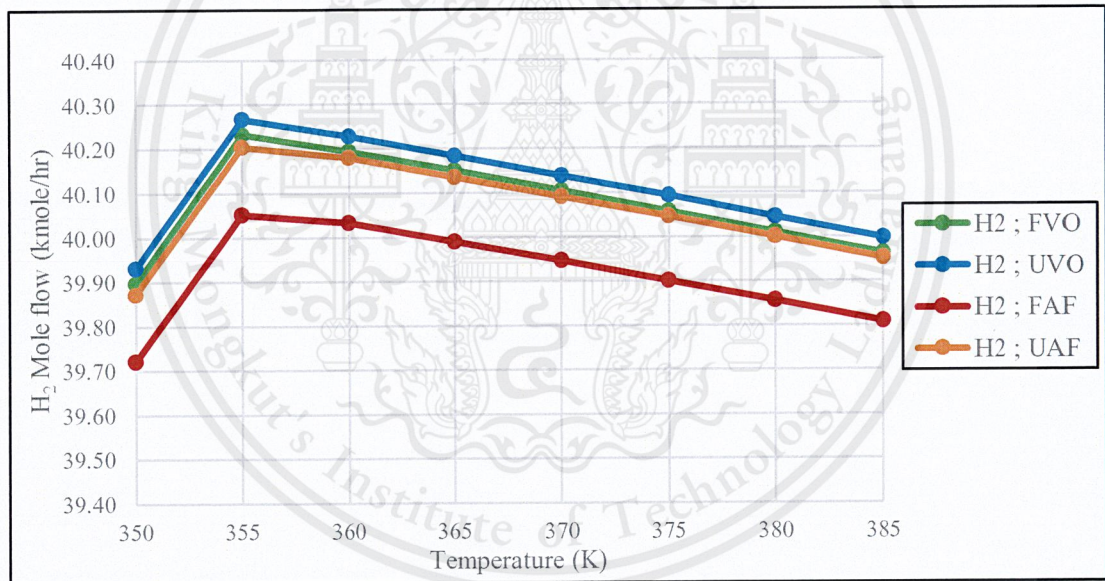


Figure 4.9. Effects of changing the temperature and type of cooking oils in ATR reactor on hydrogen mole flow.

CHAPTER V

CONCLUSION AND SUGGESTION

5.1 Conclusion

This project presents hydrogen production through autothermal reforming integrated with chemical looping by using different cooking oil, i.e., fresh and used vegetable oil and fresh and used animal fat. This study uses soybean oil as vegetable oil and lard as animal fat. The effect of operating conditions in reformer and absorber are investigated to determine the optimal conditions. The results showed that the optimal operating conditions of reformer are at temperature of 900 K, pressure of 1 bar and steam to carbon molar ratio of 5. The water gas shift reactor should be operated at 360 K and atmospheric pressure. Finally, temperature of 660 K at atmospheric pressure and amount of calcium oxide of 18 kmole/hr are the optimal operating conditions of absorber. The parameter was used to simulation as show in table 5.1.

The simulation result indicated that used vegetable oil can produce the highest amount of hydrogen, followed by fresh vegetable oil, used animal fat, and fresh animal fat. Under these operating conditions, the hydrogen purity of 99.9% can be provided and this can be used as fuel in industries.

5.2 Suggestion

1. Study on used cooking oil contaminants, i.e., tar, char and other before entering reformer.
2. Study on the economic feasibility and internal design of the hydrogen production process from cooking oil.
3. Study on the relationship between oxygen content and energy consumption of the autothermal reforming reactor.

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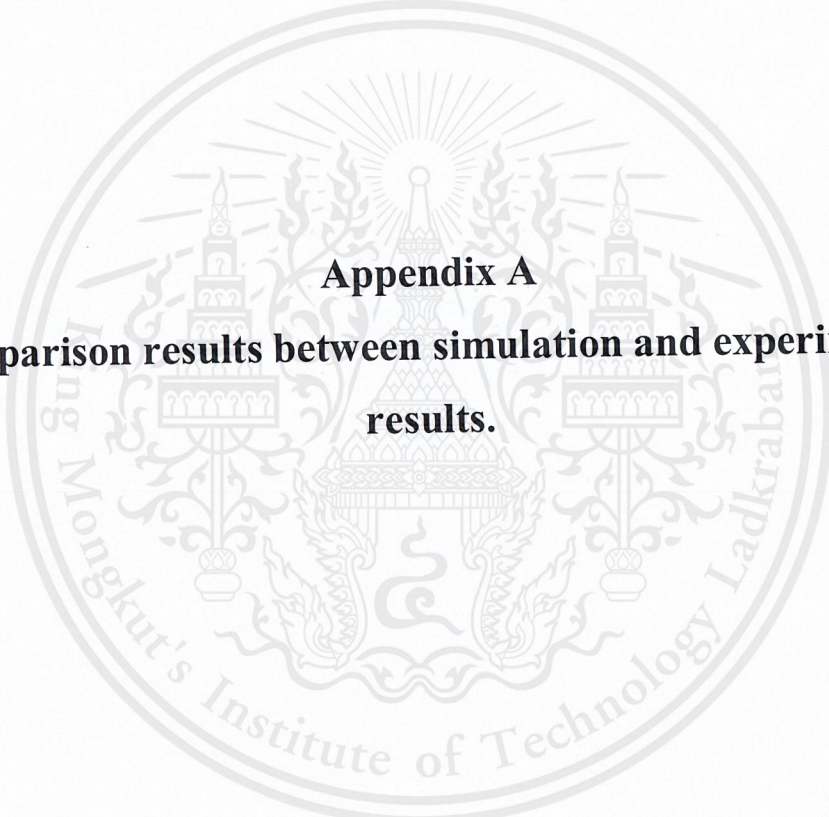
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The seal of King Mongkut's Institute of Technology Ladkrabang is a circular emblem. It features a central sunburst with rays emanating from a central point. Below the sunburst are two traditional Thai stupas (chedis) flanking a central, more ornate structure. The entire emblem is surrounded by a decorative border. The text "King Mongkut's Institute of Technology Ladkrabang" is written in a circular path around the inner edge of the seal.

Appendix A
Comparison results between simulation and experimental
results.

Table A.1 Comparison results between simulation and experimental results.

Water flow rate (ml/hr)	Mole flow (kmole/hr)									
	Hydrogen mole flow		Methane mole flow		Carbonmonooxide mole flow		Carbon dioxide mole flow			
	Experiment	Model	Experiment	Model	Experiment	Model	Experiment	Model	Experiment	Model
25	18.0000	17.3238	1.0500	1.6000	15.2000	16.2000	4.4000	3.2021		
100	18.7000	17.9230	1.5000	1.4200	14.0000	14.6150	5.2000	6.7734		
300	20.0000	19.1409	1.0000	1.2000	11.0000	12.2300	8.0000	8.9378		
440	20.0000	19.4206	1.0000	1.0000	9.0000	9.5000	9.2000	10.3870		
800	19.5000	19.3928	0.9000	0.9000	6.4000	6.2740	10.7000	11.4250		

Note: Operate under the same conditions.

Type of cooking oil:

Used vegetable oil (Soybean oil)

Temperature of reformer (T_{ATR}):

900 K

Pressure of reformer (P_{ATR}):

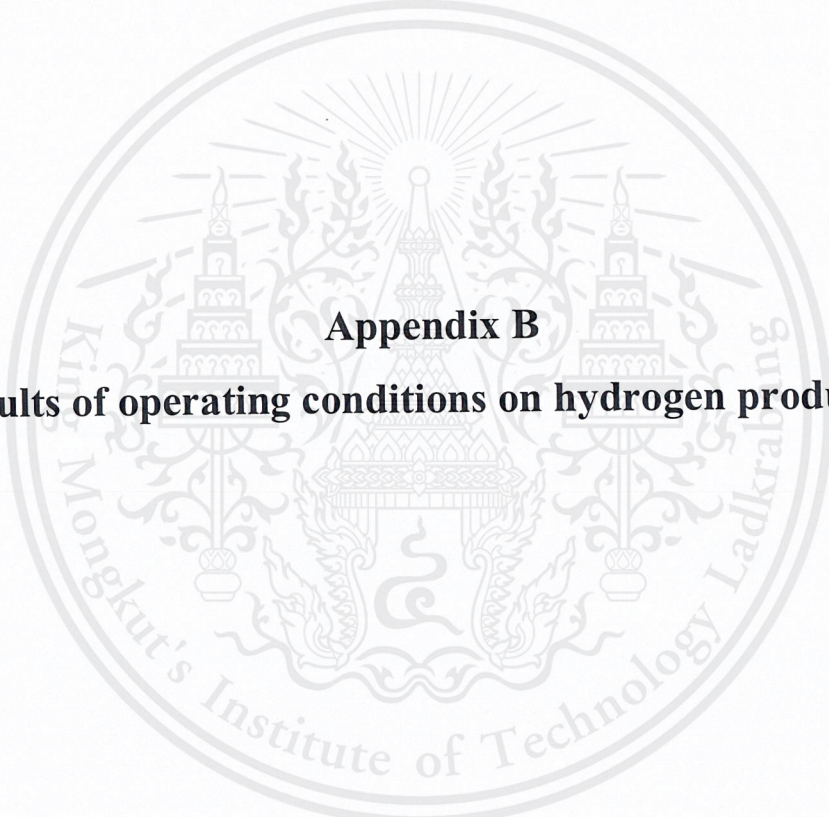
1 bar

Steam to carbon molar ratio (S/C):

1

Oxygen flow rate:

369.84 NL/hr



Appendix B
Results of operating conditions on hydrogen production

Table B.1 Results of process simulation in reformer with reformer temperature and pressure were considered

Temperature (K)	Pressure (bar)	Autothermal reforming reactor					
		Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
800	1	0.2803	0.0173	0.5652	0.0143	0.1230	
800	2	0.2393	0.0307	0.6021	0.0109	0.1170	
800	3	0.2134	0.0391	0.6255	0.0090	0.1129	
800	4	0.1952	0.0450	0.6420	0.0078	0.1100	
800	5	0.1814	0.0495	0.6544	0.0070	0.1077	
850	1	0.3105	0.0055	0.5385	0.0229	0.1227	
850	2	0.2853	0.0141	0.5611	0.0197	0.1198	
850	3	0.2640	0.0213	0.5803	0.0172	0.1172	
850	4	0.2469	0.0270	0.5956	0.0154	0.1150	
850	5	0.2331	0.0317	0.6080	0.0140	0.1132	
900	1	0.3169	0.0013	0.5333	0.0302	0.1183	
900	2	0.3077	0.0046	0.5416	0.0286	0.1175	
900	3	0.2964	0.0085	0.5516	0.0269	0.1165	
900	4	0.2853	0.0125	0.5616	0.0252	0.1155	
900	5	0.2748	0.0161	0.5710	0.0236	0.1145	
950	1	0.3140	0.0003	0.5365	0.0364	0.1128	
950	2	0.3115	0.0012	0.5387	0.0359	0.1126	
950	3	0.3077	0.0026	0.5421	0.0351	0.1124	
950	4	0.3030	0.0043	0.5463	0.0343	0.1121	

950	5	0.2978	0.0062	0.5509	0.0333	0.1118
1000	1	0.3091	0.0001	0.5415	0.0421	0.1072
1000	2	0.3084	0.0003	0.5421	0.0420	0.1072
1000	3	0.3073	0.0007	0.5431	0.0417	0.1072
1000	4	0.3058	0.0013	0.5444	0.0414	0.1071
1000	5	0.3040	0.0020	0.5460	0.0410	0.1070

Note:

Type of cooking oil:

Used vegetable oil (Soybean oil)

Oil flow rate:

1 kmole/hr

Steam to carbon molar ratio (S/C):

5

Oxygen to carbon molar ratio (O/C):

1

Table B.2 Results of process simulation in reformer with steam to carbon molar ratio was considered

Autothermal reforming reactor						
Steam to carbon molar ratio (S/C)	Mole flow rate (kmol/hr)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
1	27.1145	0.0584	6.0438	14.5012	3.2275	
2	30.8759	0.0114	19.3764	10.9279	6.8478	
3	33.0810	0.0041	34.1859	8.7520	9.0310	
4	34.5449	0.0018	49.7264	7.2970	10.4883	
5	35.5891	0.0010	65.6841	6.2563	11.5298	

Note:

Type of cooking oil:

Oil flow rate:

Oxygen to carbon molar ratio (O/C):

Temperature of reformer (T_{ATR}):

Pressure of reformer (P_{ATR}):

Used vegetable oil (Soybean oil)

1 kmole/hr

1

900 K

1 bar

Table B.3 Results of process simulation in water gas shift reactor with temperature and pressure were considered

Autothermal reforming reactor						
Temperature (K)	Pressure (bar)	Mole fraction				
		Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide
330	1	38.0983	0.1597	11.5732	3.1073	14.4303
330	2	35.6483	0.1593	4.9922	5.5464	11.8746
330	3	33.9679	0.1588	3.1147	7.2118	10.1099
330	4	32.7371	0.1584	2.2394	8.4248	8.8108
330	5	31.7937	0.1579	1.7377	9.3483	7.8111
340	1	39.1252	0.1598	21.1750	2.0822	15.4907
340	2	37.0200	0.1594	8.5624	4.1793	13.2876
340	3	35.4659	0.1591	5.2533	5.7220	11.6510
340	4	34.2668	0.1587	3.7468	6.9071	10.3817
340	5	33.3110	0.1582	2.8924	7.8468	9.3658
350	1	39.9300	0.1599	41.1097	1.2789	16.3298
350	2	38.1611	0.1596	14.6388	3.0418	14.4721
350	3	36.7739	0.1592	8.7247	4.4203	13.0068
350	4	35.6539	0.1589	6.1442	5.5294	11.8180
350	5	34.7289	0.1585	4.7086	6.4417	10.8319
360	1	40.2275	0.1599	60.7277	0.9821	16.6451
360	2	39.0978	0.1597	25.5292	2.1081	15.4534

360	3	37.8883	0.1594	14.4447	3.3110	14.1716
360	4	36.8735	0.1591	9.9594	4.3173	13.0913
360	5	36.0089	0.1588	7.5455	5.1719	12.1671
370	1	40.1378	0.1599	60.8174	1.0718	16.5554
370	2	39.8672	0.1599	47.4270	1.3415	16.2684
370	3	38.8267	0.1596	24.2949	2.3769	15.1619
370	4	37.9259	0.1594	16.1495	3.2712	14.1999
370	5	37.1376	0.1591	12.0079	4.0516	13.3549
380	1	40.0440	0.1599	60.9112	1.1656	16.4616
380	2	40.0440	0.1599	60.9112	1.1656	16.4616
380	3	39.6168	0.1598	42.9306	1.5908	16.0051
380	4	38.8268	0.1596	26.6833	2.3757	15.1587
380	5	38.1199	0.1593	19.2168	3.0764	14.3987

Note:

Type of cooking oil:

Used vegetable oil (Soybean oil)

Oil flow rate:

1 kmole/hr

Steam to carbon molar ratio (S/C):

5

Oxygen to carbon molar ratio (O/C):

1

Temperature of reformer (T_{ATR}):

900 K

Pressure of reformer (P_{ATR}):

1 bar

Table B.4 Results of process simulation in absorber with temperature and amount of calcium oxide were considered

Autothermal reforming reactor						
CaO (kmole/hr)	Temperature (K)	Mole fraction				Carbon dioxide
		Hydrogen	Methane	Steam	Carbon monoxide	
16	600	0.3488	0.0180	0.6332	0.0000	0.0000
16	620	0.3489	0.0179	0.6332	0.0000	0.0000
16	640	0.3490	0.0179	0.6330	0.0000	0.0001
16	660	0.3494	0.0178	0.6326	0.0000	0.0002
16	680	0.3504	0.0174	0.6316	0.0000	0.0005
16	700	0.3526	0.0167	0.6295	0.0001	0.0011
16	720	0.3568	0.0154	0.6254	0.0002	0.0023
16	740	0.3633	0.0133	0.6189	0.0004	0.0041
16	760	0.3716	0.0106	0.6107	0.0007	0.0064
16	780	0.3803	0.0077	0.6021	0.0011	0.0088
16	800	0.3880	0.0051	0.5945	0.0016	0.0107
17	600	0.3851	0.0078	0.6070	0.0000	0.0000
17	620	0.3851	0.0078	0.6070	0.0000	0.0000
17	640	0.3852	0.0078	0.6070	0.0000	0.0000
17	660	0.3853	0.0078	0.6069	0.0000	0.0001
17	680	0.3856	0.0077	0.6066	0.0000	0.0001
17	700	0.3862	0.0075	0.6060	0.0000	0.0003
17	720	0.3875	0.0071	0.6046	0.0001	0.0007

17	740	0.3899	0.0063	0.6023	0.0001	0.0014
17	760	0.3934	0.0051	0.5988	0.0003	0.0024
17	780	0.3975	0.0038	0.5947	0.0005	0.0035
17	800	0.4013	0.0025	0.5909	0.0007	0.0045
18	600	0.4119	0.0004	0.5877	0.0000	0.0000
18	620	0.4119	0.0004	0.5877	0.0000	0.0000
18	640	0.4119	0.0004	0.5877	0.0000	0.0000
18	660	0.4120	0.0004	0.5877	0.0000	0.0000
18	680	0.4120	0.0003	0.5877	0.0000	0.0000
18	700	0.4120	0.0003	0.5876	0.0000	0.0000
18	720	0.4120	0.0003	0.5876	0.0000	0.0000
18	740	0.4120	0.0003	0.5876	0.0000	0.0001
18	760	0.4120	0.0003	0.5875	0.0000	0.0001
18	780	0.4120	0.0003	0.5874	0.0000	0.0002
18	800	0.4119	0.0003	0.5873	0.0001	0.0005

Note:

Type of cooking oil:

Oil flow rate:

Steam to carbon monoxide (S/C):

Oxygen to carbon molar ratio (O/C):

Temperature of reformer (T_{ATR}):Pressure of reformer (P_{ATR}):Temperature of water gas shift (T_{WGS}):Pressure of reformer (P_{WGS}):

Used vegetable oil (Soybean oil)

1 kmole/hr

5

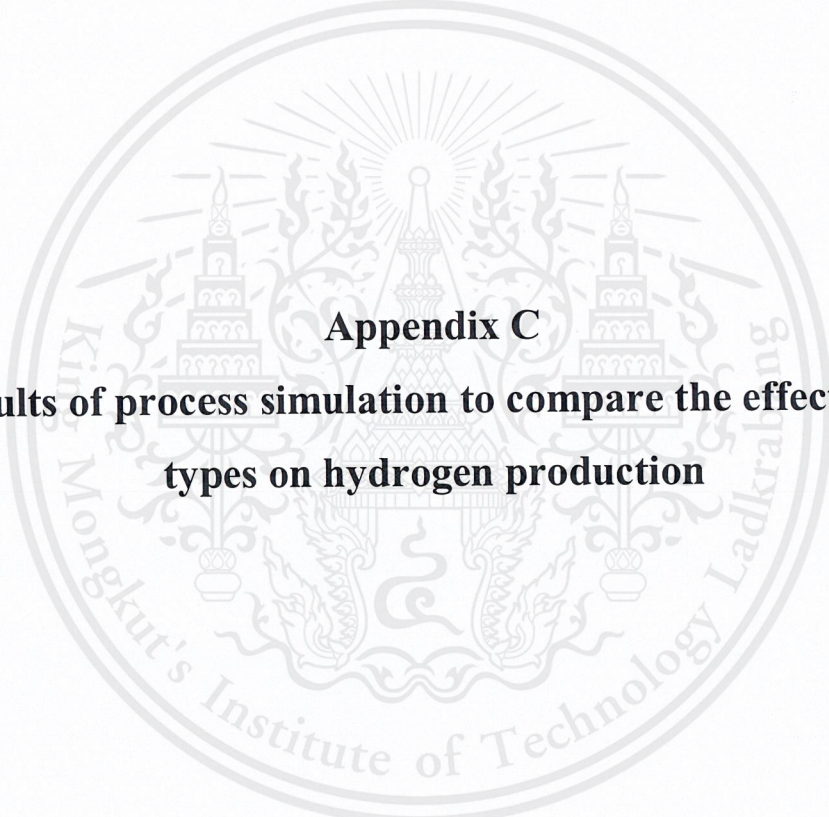
1

900 K

1 bar

360 K

1 bar

The logo of King Mongkut's Institute of Technology Ladkrabang is a circular emblem. It features a central sunburst with rays emanating from a central point. Below the sunburst are two traditional Thai stupas (chedis) flanking a central, more ornate structure. The entire emblem is surrounded by a decorative border. The text "King Mongkut's Institute of Technology Ladkrabang" is written in a circular path around the emblem.

Appendix C
Results of process simulation to compare the effect of oil
types on hydrogen production

Table C.1.1 Results of process simulation in reformer with the fresh cooking oil used as feedstock and temperature was considered

Autothermal reforming reactor: Fresh vegetable oil (FVO)						
Temperature (K)	Mole flow rate (kmol/hr)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
800	32.2359	1.9840	65.0385	1.6405	14.1605	
820	34.4189	1.3323	64.1589	2.0643	14.3884	
840	35.9837	0.8355	63.5877	2.4867	14.4628	
860	36.9477	0.4953	63.3040	2.8833	14.4064	
880	37.4336	0.2833	63.2423	3.2456	14.2560	
900	37.5967	0.1595	63.3268	3.5777	14.0478	
920	37.5659	0.0897	63.4971	3.8875	13.8077	
940	37.4267	0.0509	63.7139	4.1820	13.5521	
960	37.2297	0.0293	63.9542	4.4655	13.2901	
980	37.0032	0.0171	64.2050	4.7407	13.0271	
1000	36.7629	0.0102	64.4592	5.0088	12.7660	

Note:

Oil flow rate: 1 kmole/hr

Steam to carbon molar ratio (S/C): 5

Oxygen to carbon molar ratio (O/C): 1

Pressure of reformer (P_{ATR}): 1 bar

Table C.1.2 Results of process simulation in reformer with the use cooking oil used as feedstock and temperature was considered.

Autothermal reforming reactor: Used vegetable oil (UVO)						
Temperature (K)	Mole flow rate (kmol/hr)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
800	32.4048	1.9993	65.1736	1.6379	14.0942	
820	34.6030	1.3437	64.2866	2.0622	14.3256	
840	36.1813	0.8434	63.7090	2.4852	14.4029	
860	37.1559	0.5004	63.4204	2.8826	14.3485	
880	37.6491	0.2863	63.3553	3.2456	14.1996	
900	37.8169	0.1613	63.4377	3.5782	13.9921	
920	37.7888	0.0907	63.6068	3.8883	13.7525	
940	37.6512	0.0515	63.8229	4.1829	13.4971	
960	37.4551	0.0296	64.0627	4.4665	13.2354	
980	37.2291	0.0173	64.3133	4.7417	12.9725	
1000	36.9892	0.0103	64.5673	5.0097	12.7115	

Note:

Oil flow rate: 1 kmole/hr

Steam to carbon molar ratio (S/C): 5

Oxygen to carbon molar ratio (O/C): 1

Pressure of reformer (P_{ATR}): 1 bar

Table C.1.3 Results of process simulation in reformer with the fresh animal fat used as feedstock and temperature was considered.

Temperature (K)	Autothermal reforming reactor: fresh animal fat (FAF)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
800	32.3054	1.9204	65.6115	1.5990	13.8947	
820	34.4460	1.2826	64.7463	2.0093	14.1222	
840	35.9673	0.8004	64.1895	2.4169	14.1968	
860	36.8955	0.4728	63.9165	2.7993	14.1421	
880	37.3578	0.2697	63.8603	3.1491	13.9953	
900	37.5086	0.1517	63.9456	3.4704	13.7920	
920	37.4734	0.0853	64.1135	3.7711	13.5577	
940	37.3345	0.0484	64.3262	4.0576	13.3081	
960	37.1404	0.0279	64.5614	4.3340	13.0523	
980	36.9182	0.0163	64.8068	4.6025	12.7953	
1000	36.6827	0.0097	65.0555	4.8644	12.5400	

Note:

Oil flow rate: 1 kmole/hr

Steam to carbon molar ratio (S/C): 5

Oxygen to carbon molar ratio (O/C): 1

Pressure of reformer (P_{ATR}): 1 bar

Table C.1.4 Results of process simulation in reformer with the use animal fat used as feedstock and temperature was considered.

Temperature (K)	Autothermal reforming reactor: Used animal fat (UAF)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
800	32.3578	1.9466	65.4923	1.6108	13.9485	
820	34.5182	1.3028	64.6194	2.0254	14.1776	
840	36.0588	0.8145	64.0553	2.4378	14.2534	
860	37.0026	0.4818	63.7769	2.8249	14.1991	
880	37.4753	0.2752	63.7176	3.1788	14.0518	
900	37.6318	0.1548	63.8017	3.5037	13.8473	
920	37.5991	0.0871	63.9699	3.8073	13.6114	
940	37.4607	0.0494	64.1836	4.0963	13.3601	
960	37.2661	0.0284	64.4202	4.3749	13.1025	
980	37.0427	0.0166	64.6672	4.6455	12.8437	
1000	36.8059	0.0099	64.9175	4.9093	12.5866	

Note:

Oil flow rate: 1 kmole/hr

Steam to carbon molar ratio (S/C): 5

Oxygen to carbon molar ratio (O/C): 1

Pressure of reformer (P_{ATR}): 1 bar

Table C.2.1 Results of process simulation in reformer with the fresh vegetable oil used as feedstock and S/C was considered.

Autothermal reforming reactor: Fresh vegetable oil (FVO)						
Steam to carbon molar ratio (S/C)	Mole flow rate (kmol/hr)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
1	27.0827	0.0582	6.0433	14.4967	3.2300	
2	30.8444	0.0113	19.3754	10.9226	6.8510	
3	33.0493	0.0040	34.1850	8.7468	9.0341	
4	34.5128	0.0018	49.7259	7.2921	10.4910	
5	35.5566	0.0010	65.6839	6.2519	11.5321	

Note:

Oil flow rate:

1 kmole/hr

Oxygen to carbon molar ratio (O/C):

1

Temperature of reformer (T_{ATR}):

900 K

Pressure of reformer (P_{ATR}):

1 bar

Table C.2.2 Results of process simulation in reformer with the use vegetable oil used as feedstock and S/C was considered.

Autothermal reforming reactor: Fresh vegetable oil (UVO)						
Steam to carbon molar ratio (S/C)	Mole flow rate (kmol/hr)					
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide	
1	27.3541	0.0585	6.1059	14.4518	3.2211	
2	31.0904	0.0114	19.4638	10.9039	6.8162	
3	33.2846	0.0041	34.2843	8.7391	8.9883	
4	34.7429	0.0019	49.8304	7.2897	10.4399	
5	35.7839	0.0010	65.7912	6.2523	11.4783	

Note:

Oil flow rate:

1 kmole/hr

Oxygen to carbon molar ratio (O/C):

1

Temperature of reformer (T_{ATR}):

900 K

Pressure of reformer (P_{ATR}):

1 bar

Table C.2.3 Results of process simulation in reformer with the fresh animal fat used as feedstock and S/C was considered

Autothermal reforming reactor: Fresh Animal fat (FAF)					
Steam to carbon molar ratio (S/C)	Mole flow rate (kmol/hr)				
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide
1	27.2862	0.0546	6.3621	14.0812	3.2784
2	30.9277	0.0108	19.8082	10.6149	6.7885
3	33.0665	0.0039	34.6833	8.5038	8.9064
4	34.4873	0.0018	50.2667	7.0915	10.3209
5	35.5011	0.0009	66.2546	6.0811	11.3322

Note:

Oil flow rate:

1 kmole/hr

Oxygen to carbon molar ratio (O/C):

1

Temperature of reformer (T_{ATR}):

900 K

Pressure of reformer (P_{ATR}):

1 bar

Table C.2.4 Results of process simulation in reformer with the use animal fat used as feedstock and S/C was considered.

Autothermal reforming reactor: Used animal fat (UAF)					
Steam to carbon molar ratio (S/C)	Mole flow rate (kmol/hr)				
	Hydrogen	Methane	Steam	Carbon monoxide	Carbon dioxide
1	27.3413	0.0558	6.2902	14.1901	3.2598
2	31.0089	0.0110	19.7122	10.7018	6.7930
3	33.1635	0.0039	34.5718	8.5755	8.9264
4	34.5953	0.0018	50.1443	7.1523	10.3517
5	35.6171	0.0009	66.1242	6.1339	11.3710

Note:

Oil flow rate:

1 kmole/hr

Oxygen to carbon molar ratio (O/C):

1

Temperature of reformer (T_{ATR}):

900 K

Pressure of reformer (P_{ATR}):

1 bar

BIOGRAPHY

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